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Green-Emitting PPE−PPV Hybrid Polymers: Efficient Energy Transfer across the *m*-Phenylene Bridge

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ABSTRACT: Novel π-conjugated polymers (**7**) consisting of both poly(phenylenevinylene) (PPV) and poly(phenyleneethynylene) (PPE) blocks are synthesized by using a combination of Heck-type coupling and Horner−Wadsworth−Emmons condensation reactions. These polymers have well-defined chemical structure $(-Ph-C\equiv C-Ph-C\equiv C-Ph-C{=}C-Ph-C{=}C-)_n$, in which phenyl rings are linked alternately at meta and para positions. ^{13}C NMR spectroscopy further confirms the structural regularity of the polymers. The degree of polymerization (DP) is in the range 27−76. Resulting from efficient energy transfer from PPE block to PPV block, the PPV/PPE hybrid polymer emits light with the same color as poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)], **1**. LED devices of ITO/PPV/**7**/Ca and ITO/PEDOT/**7**/Ca configurations have been fabricated, which give green EL emission with external quantum efficiency of 0.15% for the former and 0.32% for the latter.

Introduction

π-Conjugated polymers of high electroluminescence (EL) have been a subject of great interest due to their potential application in new display technology.[1] Although many green-emitting materials have been reported, efficient ones with high brightness are still rare. One of the challenges in the field is to improve the luminescence efficiency of the existing materials without altering their emissive color. Both poly(phenylenevinylene) (PPV)[1,2] and poly(phenyleneethynylene) (PPE)[3,4] derivatives have been shown to be useful as active layers in light-emitting diodes (LEDs). Synthesis of their hybrid PPV/PPE copolymers has also been independently reported by the group of Bunz[5] and Egbe[6,7] to give poly[(*p*-phenylenevinylene)-*co*-(*p*-phenyleneethynylene)] derivatives, in which all phenyl groups are linked at the para position. In the hybrid, both PPE and PPV blocks form an integrated chromophore of no clear boundary. Although the hybrid copolymers exhibit relatively high fluorescence quantum efficiency in solution, little is known about their EL properties.[7]

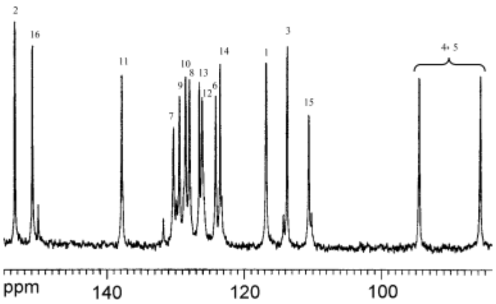

Figure 1. ^{13}C NMR spectrum of copolymer **7aa** in $CDCl_3$. The alkyl region is not shown for clarity. The ^{13}C peaks are assigned as labeled in the polymer structure **7**.

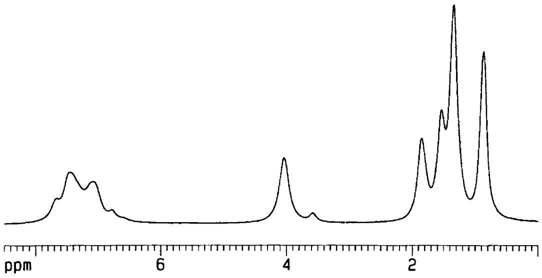

Figure 2. ^1H NMR spectrum of **7aa** in $CDCl_3$ solvent.

Our recent studies have shown that both polymers **1**[8] and **2**[9] are highly fluorescent materials. Resulting from the effective π-conjugation interruption at *m*-phenylene, the chromophores in **1** and **2** can be represented by molecular fragments **3** and **4**, respectively. Comparison between the optical properties of **1** and **2** shows that the emission of the high-energy chromophore **4** (emission maximum at ~406 nm) overlaps very well with the absorption of the low-energy chromophore **3** between 350 and 450 nm (Figure 3), thereby forming an ideal donor−acceptor pair for energy transfer.[10] The clear chromophore boundary at *m*-phenylene linkages, which cannot be achieved by using only *p*-phenylene, may play a positive role in the exciton confinement. In addition, an isolated emitter will have less tendency to form aggregate, which leads to formation of weakly emissive interchain species in thin films and significantly reduces the luminescence quantum efficiency of LED devices.[11,12] Reasoning that proper combination of both chromophores **3** and **4** in a single polymer chain could produce new materials with improved luminescence, we decide to explore the synthesis of their hybrid, i.e., PPV/PPE copolymer **7**, in which chromophores **3** and **4** are bridged via sharing a common *m*-phenylene for intimate contact (Scheme 1). The present molecular architecture partially overlaps molecular orbitals of two different chromophores, which any other intermolecular interaction cannot match, further facilitating the desirable energy migration. Study of **7** with distinguishable

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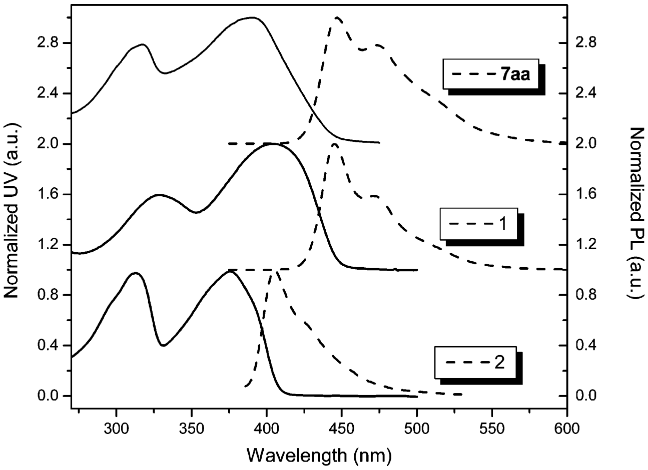
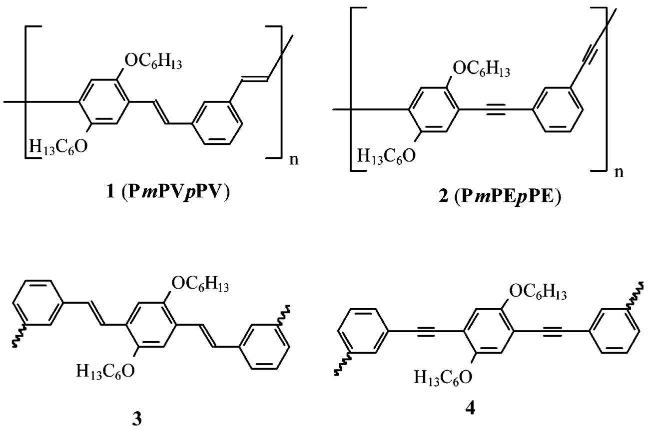


Figure 3. UV−vis absorption (solid line) and emission (dotted line) spectra of homopolymers **1** and **2** and PPV−PPE copolymer **7** in THF solution at room temperature. The fluorescence spectra were acquired while the polymer solutions were excited at 375 nm.

Chart 1



1 (P*m*PV*p*PV)

2 (P*m*PE*p*PE)

3

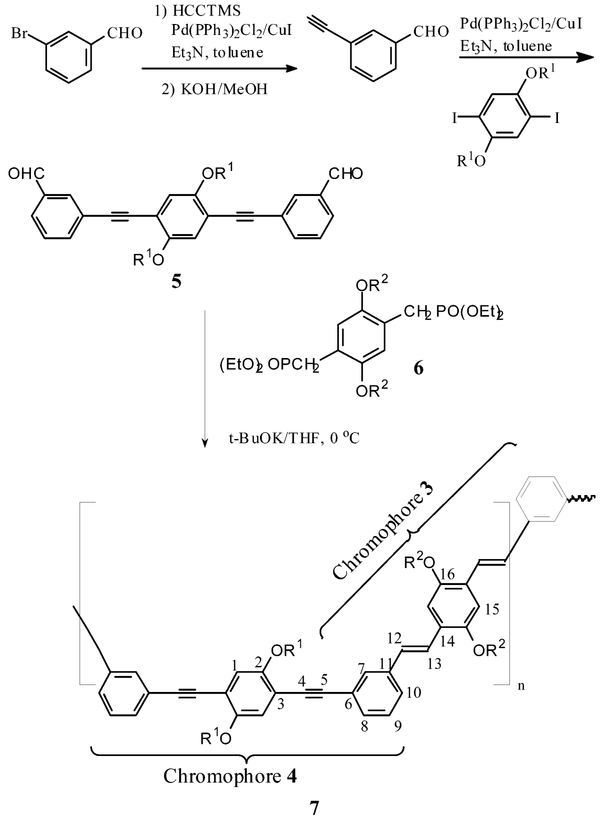
4

PPE and PPV blocks will provide useful information to understand the optical behavior of the hybrid material.

Results and Discussion

Polymer Synthesis and Characterization. The desired dialdehyde monomer **5** was obtained by reacting 3-ethynylbenzaldehyde with 1,4-diiodo-2,5-dialkoxybenzene in the presence of the palladium catalyst. Construction of ethynyl bond in the monomer synthesis step would minimize or eliminate possible contamination of polymer from butadiyne unit (−C≡C−C≡C−), which is often formed as a byproduct during the coupling reaction. Horner−Wadsworth−Emmons condensation[13] between dialdehyde **5** and bisphosphonate **6** provided copolymer **7** with vinylene in the trans configuration. The polymers exhibited good solubility in common organic solvents such as tetrahydrofuran (THF), toluene, and chloroform. Size exclusion chromatography (SEC) analysis, which was equipped with refractive index, viscosity, and light-scattering detectors, showed that the polymer had moderately high molecular weights with the degree of polymerization $n \approx 27-76$ (Table 1). A uniform thin film could be conveniently cast from their solutions.

Scheme 1. Synthesis of Hybrid Copolymer



7aa : $R^1 = (CH_2)_5CH_3$, $R^2 = (CH_2)_5CH_3$
7bb : $R^1 = (CH_2)_{11}CH_3$, $R^2 = (CH_2)_{11}CH_3$
7ab : $R^1 = (CH_2)_5CH_3$, $R^2 = (CH_2)_{11}CH_3$
7ba : $R^1 = (CH_2)_{11}CH_3$, $R^2 = (CH_2)_5CH_3$

Table 1. Polymerization and Molecular Weights of PPE/PPV Hybrid Polymers

polymer	content[a] of *trans*-CH=CH (%)	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	DP	yield (%)
7aa	92	80 500	1.36	73	82
7bb	93	84 700	1.40	53	85
7ab	96	46 000	1.72	27	80
7ba	95	117 200	1.59	76	88

[a] The content of *trans*-CH=CH was estimated from ^1H NMR spectra.

Spectroscopic studies of polymer **7** confirmed the proposed chemical structure. Infrared spectroscopy of **7** detected no absorption at about 2700 and 1700 cm^{-1} for terminal aldehyde. Observation of a band at 963 cm^{-1} in medium intensity (*trans*-CH=CH) and a very weak band at 892 cm^{-1} (*cis*-CH=CH) suggested that the olefin was predominately present in the trans configuration. The quantitative ^{13}C NMR spectrum of **7** further showed that the polymer had a regular structure. The ^{13}C NMR resonance signals were assigned as labeled in Figure 1 on the basis of polymers **1**[8,14] and **2**.[9] Only two acetylenic carbons were observed in a ratio of 1:1, further confirming the absence of butadiyne −C≡C−C≡C− impurity. Two major signals at 153.4 and 150.9 ppm were attributed to the characteristic aromatic carbons attached to the alkoxy substituents. The minor ^{13}C NMR signal at 150.03 ppm was not due to the end group, but indicative of the small amount of *cis*-CH=CH linkage along the polymer chain. The result was in agreement with its ^1H NMR spectrum (Figure 2), which detected a major (at ~4.01 ppm) and a minor (at ~3.55 ppm) −*OCH*$_2$− signal. These −*OCH*$_2$− signals are related to *cis*- and *trans*-olefins[8] and used to determine the relative content of *cis*-CH=CH (~3−8%) in the polymer.

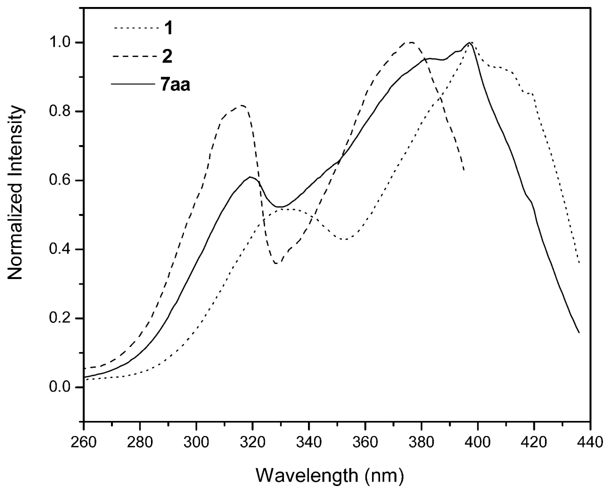


Figure 4. Excitation spectra of of **2**, **1**, and **7aa** in THF solution.

Photoabsorption and Photoluminescence. UV−vis absorption of **7** in THF (Figure 3) showed two peaks ($\lambda_{\max} \approx$ 317 and 391 nm), which are located between polymers **1** ($\lambda_{\max} \approx$ 329 and 404 nm) and **2** ($\lambda_{\max} \approx$ 313 and 376 nm). This was because the absorption of **7** resulted from a combination of two chromophores **3** and **4**, which were individually present in the corresponding homopolymers **1** and **2**. The fluorescence spectrum of **7** in THF solution, however, exhibited emission peaks with $\lambda_{\max} \approx$ 446 and 473 nm, which were essentially the same as that of **1** (emission $\lambda_{\max} \approx$ 445 and 471 nm). A very similar emission profile and energy between **1** and **7** suggested that the emission occurred only from chromophore **3**, indicating an efficient energy transfer from chromophore **4** to **3**. To further confirm the presence of energy transfer, the polymer solution was excited at ∼375 nm, which is near the absorption peak of chromophore **4**. The same emission spectra were obtained from **7** while tuning the excitation wavelength at 375 and 405 nm, supporting the assumption of efficient energy transfer.

Excitation spectra of **1**, **2**, and **7** revealed more evidence for energy transfer. As shown in Figure 4, the excitation band of copolymer **7** was significantly broader than that of homopolymers **1** and **2**. The excitation band of **7** exhibited a shoulder at about 380 nm, which is very similar in energy to that of **2** and indicates the presence of a high band-gap chromophore (PPE fragment **4**). The excitation spectrum of **7** also showed a peak at 397 ppm, which is nearly identical to that of **1** and corresponds to the second chromophore (low band-gap, PPV fragment **3**). In the excitation spectrum of **7**, similar intensities at 380 and 397 nm indicate that both chromophores **3** and **4** can be excited equally well under the photon irradiation condition used. Irradiation of the polymer solution at ∼380 and 397 nm gave the same fluorescence spectrum as shown in Figure 3. In addition to the identical emission profile observed from **7** and **1**, the result further supports the assumption that the emission occurred only from the low-band-gap chromophore as a result of efficient energy transfer from PPE to PPV fragments.

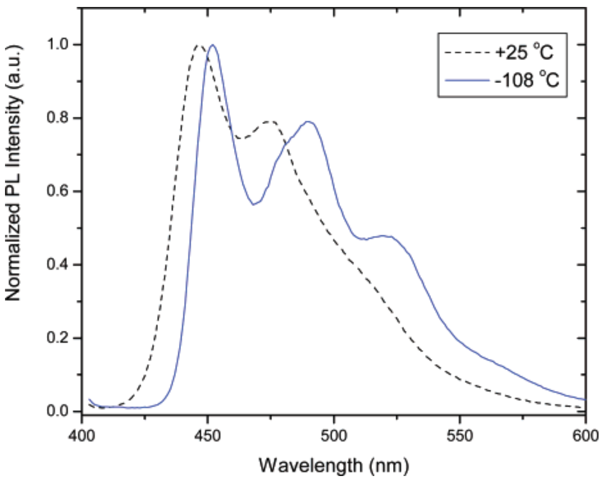


Figure 5. Fluorescence spectra of **7aa** at 25 and −108 °C.

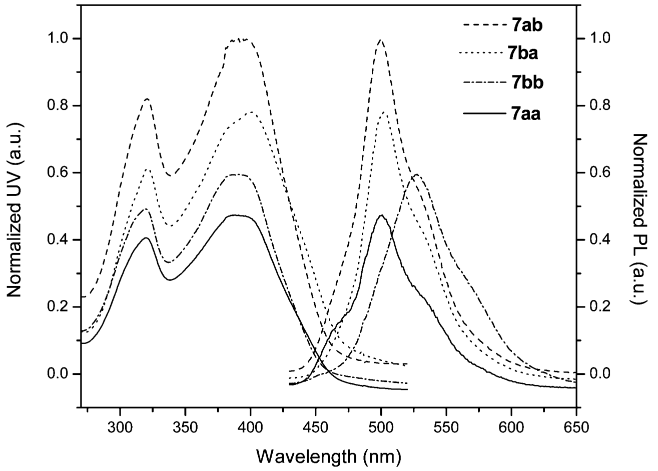


Figure 6. UV−vis absorption and emission spectra of films **7** on quartz substrates are normalized to same scale. The spectra of different polymer films are slightly offset for clarity.

Figure 5 shows the fluorescence spectra of **7** at room and low temperature. As temperature was lowered to −108 °C, the vibronic bands became more resolved, showing emission peaks at 452, 490, and 524 nm (corresponding to the wavenumber of 22 124, 20 408, and 19 084 cm^{-1}, respectively). The observed vibronic structure appears to fit the model of an anharmonic oscillator with a wavenumber separation of ∼1716 cm^{-1}, which is comparable to that of ∼1659 cm^{-1} observed from **1**.[15] The result shows that the vibronic structure of **7** in the ground-state retains the same vibrational characteristics as that of **1**.

Figure 6 shows the absorption and emission spectra of films **7** spin-cast on quartz plates. The emission $\lambda_{\max}$ of film **7** is located near 500 nm, which is about the same as that of film **1**. The absorption spectra of film **7** exhibit two bands with $\lambda_{\max}$ at about 321 and 395 nm, which are notably blue-shifted (by about 20 nm) from that of film **1** (Table 2). The blue-shifted absorption helps to reduce the overlapping area between the absorption and emission spectra of film **7**, which is consistent with what observed in the solution spectra (Figure 3). Emission of film **7bb** is red-shifted by ∼30 nm from that of film **7aa**, **7ab**, and **7ba**, indicating the influence of side chain length and arrangement to the optical properties. The copolymer **7** emitted strongly from both solution and film states. The fluorescence quantum efficiency of **7** in THF was estimated to be about 0.5, which was lower than that of **1** but higher than that of **2**. Direct comparison between films **7** and **1** showed that the former emitted about 1.4 times as intense as the latter.

EL Properties. The observed high fluorescence efficiency in the film state indicated potential use of

Table 2. UV−Vis Absorption and Photoluminescence of Copolymer 7

	UV, λ_{max} (nm)[a]		PL, λ_{max} (nm)[a]		
polymer	solution	film	solution	film	ϕ_{fl}
7aa	317, **391**	320, **394**	**446**, 476 (sh)	464 (sh), **500,** 536 (sh)	0.55
7ab	317, **391**	320, **394**	**446**, 475 (sh)	**501**, 535 (sh)	0.56
7ba	317, **391**	321, **401**	**446**, 473 (sh)	**500**, 530 (sh)	0.54
7bb	317, **391**	320, **393**	**446**, 473 (sh)	528	0.55
1	329, **404**	330, **415**	**444**, 475 (sh)	**505**, 535 (sh)	0.60
2	313, **376**	316, **383**	**405**, 428 (sh)	**471**, 495 (sh)	0.44

[a] The bold number indicates the most intense peak. The solution data were obtained by dissolving polymers in THF solvent.

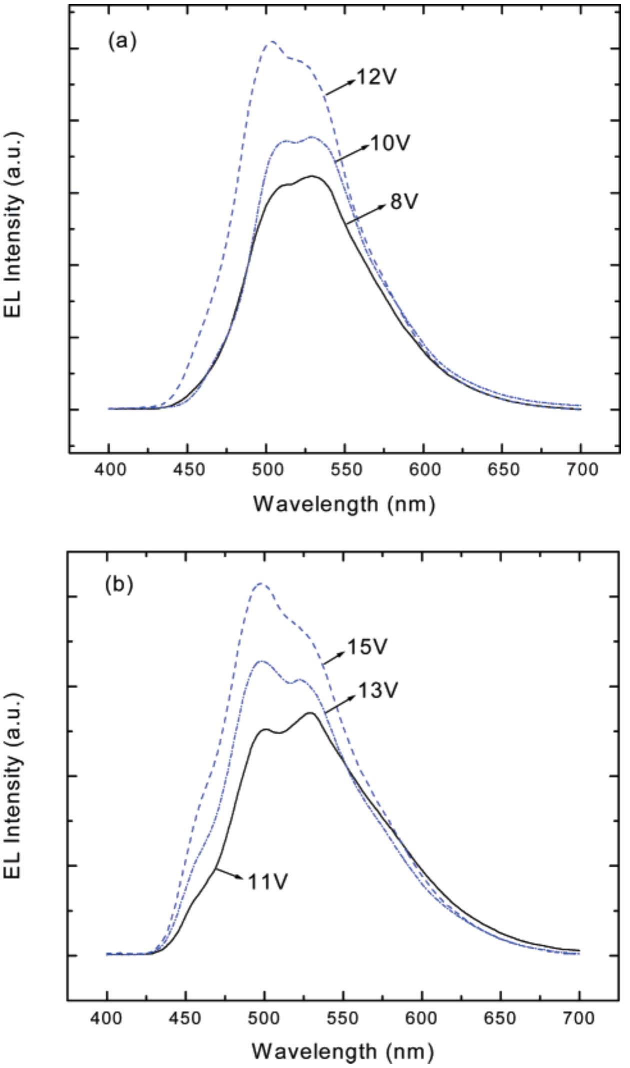


Figure 7. EL spectra for device ITO/PPV/**7aa**/Ca (top) and ITO/PEDOT/**7aa**/Ca (bottom) at different voltages.

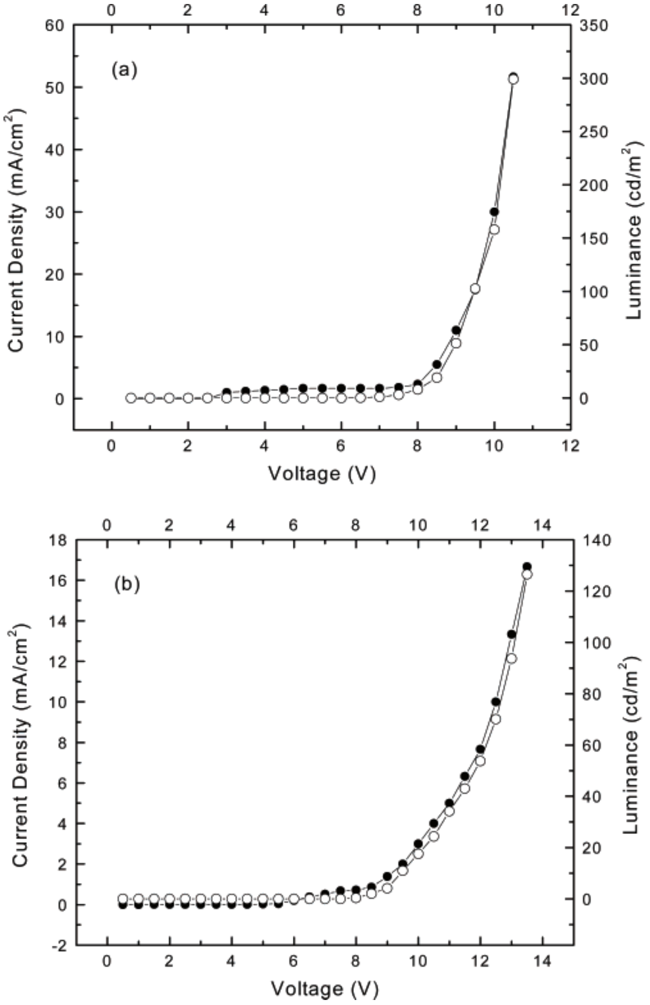


Figure 8. Current density (●)−voltage−luminance (○) relationship for device ITO/PPV/**7aa**/Ca (a) and ITO/PEDOT/**7aa**/Ca (b).

polymer **7** as an emissive layer in LED devices. To test this hypothesis, a device of ITO/PPV/**7**/Ca configuration was fabricated. The device gave pure green electroluminescence (EL) with a turn-on voltage of about 8 V. While an external voltage of 8−10 V was applied to the device, the EL emission maxima were centered near λ_{max} ≈ 513 and 529 nm (Figure 7a). As the applied voltage was raised to 12 V, the emission was slightly blue-shifted to about 504 and 522 nm, showing that the EL spectrum was slightly dependent on the voltage used. The same trend was also observed from the device of ITO/PEDOT/**7aa**/Ca (Figure 7b), with the EL emission λ_{max} ≈ 501 and 529 nm at 11 V and λ_{max} ≈ 498 and 523 nm at 15 V. The blue shift in EL at higher voltage could be due to Joule heating in the LED, which results in thermochromism.[16] This phenomenon might also result from band-gap distribution in the polymer.[17] At higher applied voltage, the high-band-gap segments in the polymer appeared to contribute slightly more to the emission. The EL spectra from both device configurations matched well with the film PL spectrum of **7aa**, indicating that both PL and EL originated from the same radiative decay process of the singlet exciton.[18] The device of ITO/PPV/**7**/Ca had an external quantum efficiency of 0.15%, which is much higher than that of **2** and comparable to that of **1**.[15] Current density−voltage-luminance characteristics (Figure 8) showed that the injection of electrons and holes in the device remained to be balanced as observed in **1**, suggesting that presence of PPE block in the PPV/PPE copolymer had little influence on the charge carrier injection. With the device configuration of ITO/PEDOT/**7**/Ca, the EL efficiency increased to 0.32% as a direct result of quite lower current density. The higher PL efficiency of film **7** than that of film **1** suggests that the EL efficiency of the former could be further improved.

Experimental Section

Materials and Measurements. 3-Bromobenzaldehyde and trimethylsilylacetylene were purchased from Aldrich Chemical Co. and GFS Chemical Co., respectively. 2,5-Diiodo-1,4-dialkoxybenzene[19] and 2,5-dialkoxy-*p*-xylylenebis(diethylphosphonate)[20] were prepared according to literature procedures. NMR spectra were collected on a 400 MHz Bruker ARX-400 spectrometer. Infrared spectra were acquired on a Nicolet Impact 400 FT-IR spectrometer. UV−vis spectra were acquired on a Hewlett-Packard 8453 diode array spectrophotometer. Fluorescence spectra were obtained on a PTI steady-state fluorometer. The quantum yields were measured in THF solvent by using quinine sulfate as a standard ($\phi_{\mathrm{fl}} = 0.577$).[21] The sample solutions were excited at 390 nm. Size exclusion chromatography (SEC) was carried out on a Viscotek SEC assembly consisting of a model P1000 pump, a model T60 dual detector, a model LR40 laser refractometer, and three mixed bed columns (10 μm). Polymer concentrations for SEC experiments were prepared in a concentration of about 3 mg/mL. The SEC system was calibrated prior to use by using narrow and broad polystyrene standards that were purchased from American Polymer Standards Corp.

3-Ethynylbenzaldehyde. 3-Bromobenzaldehyde (9.25 g, 50 mmol) and trimethylsilacetylene (4.91 g, 50 mmol) were dissolved in a mixture of solvents consisting of toluene (100 mL) and triethylamine (25 mL) in a 250 mL round-bottomed flask. After replacing the air with argon in the flask, $PdCl_2(PPh_3)_2$ (350 mg, 1 mol %) and $Cu(OAc)_2$ (90 mg, 2 mol %) were added. The reaction mixture was then heated at 70 °C for 20 h under a positive argon atmosphere. After cooling to room temperature, the mixture was passed through a thin layer of Celite to remove salts and catalysts, and the solvents were evaporated on a rotatory evaporator. Purification of the resulting residues on a silica gel column (eluent: ethyl acetate/hexane = 1:10) offered 3-trimethylsilylethynylbenzaldehyde (7.0 g, 70%) which was further treated for 2 h with KOH (2.0 g) in 50 mL of solvent mixture of methanol and THF (1:1) at room temperature. After recrystallization from hexanes, the desired product was obtained as crystals (4.0 g, 90%; mp = 75−76 °C), which had the following spectral properties. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.15 (s, 1H, $-C{\equiv}CH$), 7.50 (t, $J = 7.8$ Hz, 1H, Ar−H), 7.72 (d, $J = 7.8$ Hz, 1H, Ar−H), 7.85 (d, $J = 7.8$ Hz, 1H, Ar−H), 7.98 (s, 1H, Ar−H), 9.99 (s, 1H, −CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 78.65, 81.85, 123.03, 128.82, 129.22, 133.13, 136.12, 137.33, 191.08. Anal. Calcd for C_9H_6O: C, 83.06; H, 4.65. Found: C, 83.15; H, 4.54.

1,4-Bis(3-formylphenyl-1-ethynyl)-2,5-dihexyloxybenzene (**5a**). 2,5-Diiodo-1,4-dihexyloxybenzene (2.651 g, 5 mmol) and 3-ethynylbenzaldehyde (1.302 g, 10 mmol) were dissolved in a solvent mixture consisting of 5 mL of triethylamine and 50 mL of toluene. The solution was degassed under vacuum and subsequently filled with argon to remove oxygen. After addition of $PdCl_2(PPh_3)_2$ (35 mg, 1 mol %) and CuI (20 mg, 2 mol %), the reaction mixture was stirred overnight at room temperature under a positive argon atmosphere. After removing salt precipitate via filtration and solvents on a rotatory evaporator, further purification on a silica gel column (hexanes/ethyl acetate = 10:1) afforded **5a** (2.20 g, 82%) as yellowish crystals (mp = 102−103 °C). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 0.87 (t, $J = 6.8$ Hz, 6H, $-CH_3$), 1.32−1.55 (m, 12H, $-CH_2-$), 1.85 (m, 4H, $-CH_2-$), 4.04 (t, $J = 6.8$ Hz, 4H, $-OCH_2-$), 7.02 (s, 2H, Ar′−H), 7.52 (t, $J = 7.8$ Hz, 2H, Ar−H), 7.76 (d, $J = 7.8$ Hz, 2H, Ar−H), 7.83 (d, $J = 7.8$ Hz, 2H, Ar−H), 8.02 (s, 2H, Ar−H), 10.01 (s, 2H, −CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 13.76, 22.38, 25.49, 29.00, 31.31, 69.36, 87.21, 93.14, 113.51, 116.62, 124.39, 128.65, 128.83, 132.65, 136.23, 136.78, 153.47, 191.24. Anal. Calcd for $C_{36}H_{38}O_4$: C, 80.87; H, 7.16. Found: C, 80.78; H, 7.14.

1,4-Bis(3-formylphenyl-1-ethynyl)-2,5-didodecyloxybenzene (**5b**). The synthesis of **5b** was similar to that described for **5a**, using 2,5-diiodo-1,4-didodecyloxybenzene as a starting material. The product **5b**, which was needlelike crystals (mp 78.5−79.5 °C), had the following spectral properties. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 0.86 (t, $J = 7.2$ Hz, 6H, $-CH_3$), 1.22−1.55 (m, 36H, $-CH_2-$), 1.86 (m, 4H, $-CH_2-$), 4.04 (t, $J = 7.2$ Hz, 4H, $-OCH_2-$), 7.03 (s, 2H, Ar′−H), 7.52 (t, $J = 7.8$ Hz, 2H, Ar−H), 7.76 (d, $J = 7.8$ Hz, 2H, Ar−H), 7.84 (d, $J = 7.8$ Hz, 2H, Ar−H), 8.02 (s, 2H, Ar−H), 10.01 (s, 2H, −CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 13.85, 22.41, 25.83, 29.07, 29.15, 29.36, 31.63, 69.36, 87.23, 93.14, 113.53, 116.63, 124.40, 128.62, 128.82, 132.66, 136.24, 136.77, 153.47, 191.19. Anal. Calcd for $C_{48}H_{62}O_4$: C, 82.01; H, 8.89. Found: C, 82.00; H, 8.84.

Preparation of Polymer 7aa. Monomers **5a** (0.2893 g, 0.5 mmol) and 2,5-dihexoxy-*p*-xylylenebis(diethylphosphonate) (0.2673 g, 0.5 mmol) were dissolved in 10 mL of dry THF. While the solution was cooled by an ice/water bath, potassium *tert*-butoxide (1.0 M in THF, 1.2 mL, 1.2 mmol) was added dropwise via a syringe over a period of 1 h under an argon atmosphere. During the initial reaction period, a pink-red color was formed and quickly disappeared upon addition of potassium *tert*-butoxide. A steady orange color was formed at the end of addition. The reaction mixture was then further stirred overnight at room temperature. The polymer was precipitated out by dropwise addition of its THF solution into methanol (150 mL) for three times. After drying at 40 °C under vacuum for 24 h, the polymer **7aa** (0.33 g, 82%) was obtained as orange powder and had the following spectral properties. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 0.89 (br, 12H, $-CH_3$), 1.35 (br, 12H, $-CH_2-$), 1.56 (br, 8H, $-CH_2-$), 1.86 (br, 8H, $-CH_2-$), 3.57 (br, 0.32H, *cis*$-OCH_2-$); 4.05 (br, 7.68H, *trans*$-OCH_2-$), 7.01−7.14 (m, 6H, Ar−H), 7.34−7.51 (m, 8H, Ar−H), 7.69 (br, 2H, Ar−H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 13.86, 22.44, 25.60, 29.16, 31.39, 69.47, 85.71, 94.55, 110.62, 113.76, 116.85, 123.55, 124.17, 126.17, 126.58, 128.00, 128.56, 129.45, 130.31, 137.88, 150.88, 153.40. IR (film): 2930 (s), 2862 (s), 2010 (w), 1591 (m), 1504 (s), 1468 (m), 1421 (m), 1387 (m), 1203 (s), 1029 (m), 963 (m), 892 (w), 859 (w), 787 (m). Anal. Calcd for $C_{56}H_{68}O_4$: C, 83.54; H, 8.51. Found: C, 83.05; H, 8.10.

Preparation of Polymer 7ab. By using the same procedure as for **7aa**, polymer **7ab** (yield 85%) was obtained as an orange resin and had the following spectral properties. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 0.85 (br, 12H, $-CH_3$), 1.23 (br, 36H, $-CH_2-$), 1.54 (br, 8H, $-CH_2-$), 1.87 (br, 8H, $-CH_2-$), 3.57 (br, 0.52H, *cis*$-OCH_2-$), 4.05 (s, 7.48H, *trans*-OCH_2-), 7.01−7.14 (m, 6H, Ar−H), 7.34−7.51 (m, 8H, Ar−H), 7.69 (br, 2H, Ar−H). IR (film): 2922 (s), 2853 (s), 2210 (vw), 1591 (m), 1503 (m), 1466 (m), 1420 (m), 1384 (m), 1203 (m), 1302 (m), 963 (m), 891 (w), 862 (w), 786 (m). Anal. Calcd for $C_{68}H_{92}O_4$: C, 83.90; H, 9.53. Found: C, 83.15; H, 8.97.

Preparation of Polymer 7ba. Polymer **7ba** (yield 80%) was obtained as yellow powder and had the following spectral properties. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 0.88 (br, 12H, $-CH_3$), 1.24 (br, 36H, $-CH_2-$), 1.56 (br, 8H, $-CH_2-$), 1.88 (br, 8H, $-CH_2-$), 3.60 (br, 0.33H, *cis*-OCH_2-), 4.06 (s, 7.67H, *trans*-OCH_2-), 7.01−7.14 (m, 6H, Ar−H), 7.34−7.51 (m, 8H, Ar−H), 7.69 (br, 2H, Ar−H). IR (film): 2924 (s), 2855 (s), 2209 (vw), 1592 (m), 1505 (m), 1470 (m), 1423 (m), 1385 (m), 1202 (m), 1302 (m), 963 (m), 894 (w), 862 (w), 787 (m). Anal. Calcd for $C_{68}H_{92}O_4$: C, 83.90; H, 9.53. Found: C, 83.27; H, 9.07.

Preparation of Polymer 7bb. Polymer **7bb** (yield 88%) was obtained as a yellow resin and had the following spectral properties. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 0.85 (br, 12H, $-CH_3$), 1.23 (br, 64H, $-CH_2-$), 1.54 (br, 8H, $-CH_2-$), 1.87 (br, 8H, $-CH_2-$), 3.57 (br, 0.52H, *cis*-OCH_2-), 4.05 (s, 7.48H, *trans*-OCH_2-), 7.01−7.14 (m, 6H, Ar−H), 7.34−7.51 (m, 8H, Ar−H), 7.69 (br, 2H, Ar−H). IR (film): 2924 (s), 2855 (s), 2207 (vw), 1593 (m), 1503 (m), 1466 (m), 1420 (m), 1378 (m), 1202 (m), 1032 (m), 963 (m), 891 (w), 859 (w), 787 (m). Anal. Calcd for $C_{80}H_{116}O_4$: C, 84.15; H, 10.24. Found: C, 83.87; H, 9.65.

LED Device Fabrication and Measurement. PPV/ITO substrates were obtained by spin-casting sulfonium polyelectrolyte precursor polymer[2] methanol solution onto ITO glass (OFC Co.) and then doing thermal conversion to PPV under flowing argon at 250 °C for 2.5 h. PEDOT/PSS (Bayer Co.) was spin-cast onto ITO glass. The polymer solutions (20 mg/mL in chloroform) were filtered through 0.2 μm Millex-FGS Filters (Millipore Co.) and were then spin-cast onto dried PPV/ITO or PEDOT/ITO substrates under a nitrogen atmosphere. The polymer films were typically 75 nm thick. Calcium electrodes of 400 nm thickness were evaporated onto the polymer films at about 10^{-7} Torr, followed by a protective coating of aluminum. The devices were characterized using a system constructed in our laboratory described elsewhere.[22]

Conclusions

PPE–PPV hybrid copolymers **7** have been synthesized, in which the phenylenes are alternately linked at the para and meta position along the chain for reduced chain rigidity and improved morphology. Although the absorption $\lambda_{\max}$ of **7** falls between P*m*PV*p*PV **1** and P*m*PE*p*PE **2**, the emission wavelength of **7** is nearly identical to that of **1**, attributing to the efficient intramolecular energy transfer across *m*-phenylene. In addition, the vibronic structure of **7** in the ground state exhibits very similar feature as that of **1** (anharmonic oscillator), showing that the chromophore in the PPV/PPE hybrid polymer retains the emissive feature of the chromophore in **1**. In other words, placement of a PPV chromophore block between two adjacent PPE blocks has little effect on the emission wavelength of the PPV block. Blue-shifted absorption reduces the overlapping between the absorption and emission spectra, thereby alleviating the self-absorption problem during device operation. The hybrid copolymer exhibits improved luminescence in film state, partly attributing to PPV chromophore isolation. With the device configuration of ITO/PEDOT/**7**/Ca, the polymer EL efficiency increased to 0.32%. The device has a turn-on voltage of ~8 V, indicating the relatively higher charge-injection barrier. Future study will focus on modification of polymer structure to improve the charge injection characteristics of the hybrid material.

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Supporting Information Available: Infrared spectrum and SEC chromatogram of polymer **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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